Preparation, Properties and Crystal Structure of $I_{0.5}TaSe_4$

S. Kikkawa, S. Uenosono and M. Koizumi

The Institute of Scientific and Industrial Research,
Osaka University, Osaka 567, Japan

Abstract

$I_{0.5}TaSe_4$ was obtained by heating the starting mixture having compositional ratio of Se/Ta=4 and I/Ta=1 in 460°C/420°C temperature gradient for 1 week. The compound was tetragonal having lattice parameters a=9.555Å and c=12.75Å. The observed density was 5.99 g/cm^3. X-ray structural analysis showed that tantalum is coordinated with 4 Se-Se dimers forming [$TaSe_4$] infinit chain along c-axis. Iodine is located between the chain. There are two kinds of tantalum in the chain. The short distance of 3.24Å between Se and I suggests that iodine is partially transfered electrons from every two Ta through Se. The electrical resistivity along c-axis was 1.9×10^3 Ωcm at room temperature and the activation energy was 0.06 eV. Magnetic susceptibility showed very weak temperature dependence: -1.7×10^{-7} emu/g at room temperature and -1.7×10^{-8} emu/g at 77K. The presences of Ta^{4+}, Ta^{5+} and $(Se\text{-}Se)^{2-}$ were observed on X-ray photoelectron spectrum comparing with those of $TaSe_2$, $TaSe_3$ and Ta_2O_5.

Introduction

Transition metal polychalcogenides are attractive materials as low-dimensional conductors and as possible candidates for secondary battery cathodes (1, 2, 3). There have been extensive investigations on layered dichalcogenides and quasi-one-dimensional trichalcogenides. Especially the compounds of Va group metal are interesting low-dimensional conductors. There are very limitted number of polychalcogenides containing more amount of chalcogen than trichalcogenides. The mineral patronite, VS_4, has the chain structure (4). Three niobium selenides with approximate composition $NbSe_4$ were initially reported (5). However, it has recently been shown that two of these are in fact Nb_2Se_9 and $I_{0.3}NbSe_4$ (6, 7). The geometric aspects of their crystal structure show marked one-dimensional character. There have been no report on the presence of tantalum tetraselenide.

In the present manuscript, preparation of $TaSe_4$ is attempted using iodine as transporting agent below 500°C. New compound, $I_{0.5}TaSe_4$, crystallized in columnar shape. Its preparation, properties and crystal structure are described.

Experimental

Mixtures of Ta, Se and I were heated in sealed quartz tubes for 1 week. The products were characterized using X-ray powder diffractometry, fluorescent X-ray spectroscopy, TG-DTA and X-ray photoelectron spectroscopy. Electrical resistivity was measured using two-probe method. Four-circle diffractometer was used for structural determination with MoKα radiation. The crystal structure was refined using the program RFINE on 391 independent reflections.

Results and Discussion

The products from a temperature gradient of 700°C/630°C are summarized in Table 1. Equimolar iodine was added to tantalum.

Table 1. Products in Ta-Se-I system in a temperature gradient of 700°C/630°C

Ta:Se:I ratio in starting powder	Products	
	in high temp. region	in low temp. region
1:3:1	$TaSe_2$ + $TaSe_3$ + phase x	$TaSe_3$
1:4:1	$TaSe_2$ + $TaSe_3$ + phase X	phase X
1:5:1	$TaSe_2$ + $TaSe_3$ + phase X	phase X + Se

Unknown phase crystallized in the hotter end of the reaction vessel accompanying $TaSe_2$ and $TaSe_3$ at all starting compositions. The products in the colder end are $TaSe_3$ at the starting composition Se/Ta=3, the unknown phase X at Se/Ta=4 and a mixture of the unknown phase X with selenium at Se/Ta=5. Thus the compositional ratio can be estimated as Se/Ta=4 for the phase X. Then the starting mixture of Se/Ta=4 was reacted with various amount of iodine. The reaction temperature was lowered to the temperature gradient of 560°C/460°C to avoid the formation of $TaSe_2$. The phase X crystallized with iodine at the colder end and a small amount of $TaSe_3$ was obtained at the hotter end. With the increase of I/Ta ratio in starting composition from 0.3 to 0.9, the amount of phase X increased and that of $TaSe_3$ decreased in the product. Monophase of the unknown compound was obtained by heating the starting mixture having ratio Ta:Se:I=1:4:1 in a temperature gradient of 460°C/420°C for 1 week. Excess iodine was removed by washing with acetone. Black single crystals having metallic luster were obtained in columnor shape having maximum dimensions of 0.5 x 0.5 x 3 mm.

Characterization

X-ray diffraction data in Table 2 can be indexed as tetragonal having lattice parameters a=9.555Å, c=12.75Å. Chemical composition was determined as $I_{0.5}TaSe_4$ by fluorescent X-ray spectroscopy using an equimolar mixture of $TaSe_2$ and KI as standard. The observed density was 5.99 g/cm^3 and Z=8. Figure 1 shows the result of thermal analysis. $I_{0.5}TaSe_4$ is gradually oxidized above 230°C and a big exotherm and 60% weight loss were observed at 400°C. Further weight loss was not detected below 1000°C. The sample heated up to 1000°C was Ta_2O_5. Thus the iodine is not simply included as molecular iodine but tightly bound in the compound as selenium. The observed weight loss agrees well with the value expected for the oxidation of $I_{0.5}TaSe_4$ to Ta_2O_5. Electrical resistivity was measured in a temperature range of -80°C to room temperature. It is 1.9 x 10^3 Ωcm at room temperature. The compound is a diamagnetic semiconductor with activation energy E_a=0.06 eV, χ_g=-1.7 x 10^{-7} emu/g at room temperature and χ_g= -1.7 x 10^{-8} emu/g at 77K.

X-ray photoelectron spectra of Ta(4f) and Se(3d) are shown in Figs. 2 and 3. $I_{0.5}TaSe_4$ is compared with Ta_2O_5, $TaSe_2$ and $TaSe_3$. The binding energies of $4f_{7/2}$ and $4f_{5/2}$ are 26.2 eV and 27.8 eV in Ta_2O_5. They are 22.5 eV and 24.5 eV in $TaSe_2$, and 23.2 eV and 25.0 eV in $TaSe_3$. A pair of sharp peaks are observed around 23 eV and 25 eV in $I_{0.5}TaSe_4$. The values correspond to those of $TaSe_2$

Table 2. X-ray diffraction data for $I_{0.5}TaSe_4$

$d_{obs.}$	$d_{calc.}$	hkl	I/I_o
6.758	6.757	110	100
4.7780	4.7776	200	59
4.0566	4.0517	211	18
3.9002	3.8831	103	<1
3.3785	3.3783	220	12
3.0129	3.0133	213	17
2.7336	2.7304	312	15
2.5938	2.5947	321	6
2.3891	2.3888	400	18
2.3220	2.3184	224	5
2.2786	2.2801	411	5
2.2513	2.2522	330	8
2.1961	2.1929	314	15
2.1366	2.1366	420	48
2.0251	2.0259	422	9
1.8898	1.8899	501	2
1.8733	1.8739	510	12
1.7570	1.7585	521	5
1.6879	1.6880	440	5

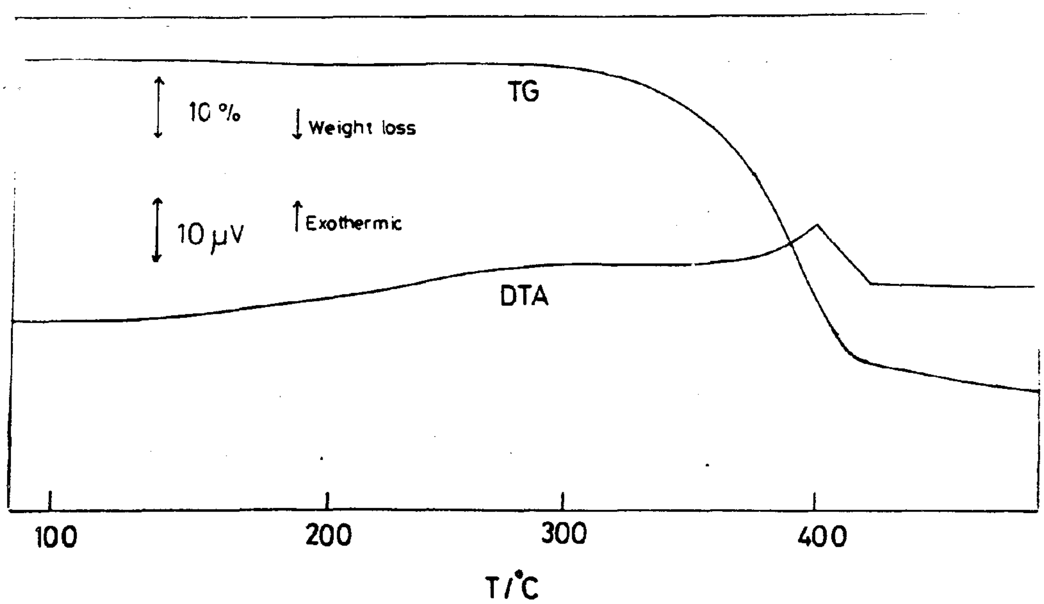

Fig. 1. TG-DTA curves for $I_{0.5}TaSe_4$

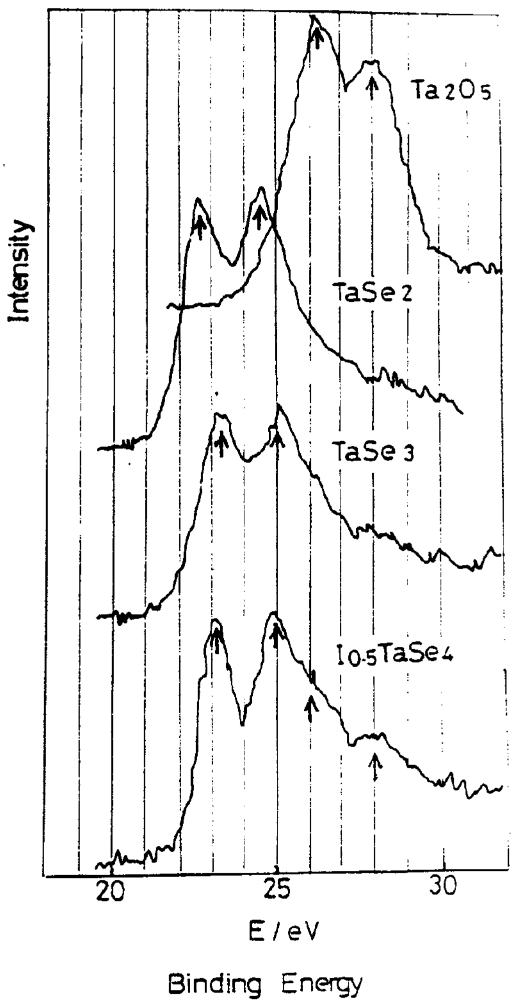

Fig. 2. X-ray photoelectron spectra of Ta(4f)

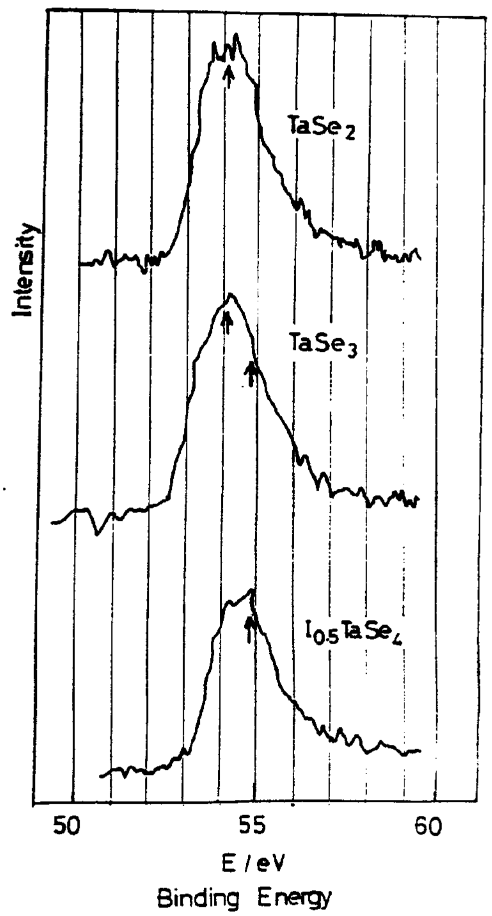

Fig. 3. X-ray photoelectron spectra of Se(3d)

and $TaSe_3$ suggesting the presence of Ta^{4+}. Another pair of broad peaks are around 26 eV and 28 eV, which agree well with those of Ta_2O_5. Thus there are two kinds of tantalum in $I_{0.5}TaSe_4$, formally tetravalent and pentavalent. $TaSe_2$ has divalent Se and its binding energy of 3d level is 54.2 eV. $TaSe_3$ has both Se^{2-} and $(Se-Se)^{2-}$ (2). It shows an asymmetric peak around 54.2 eV due to the coexistence of two kinds of selenium. The binding energy of 3d electron in $(Se-Se)^{2-}$ can be expencted as ca. 55 eV from the spectrum of $TaSe_3$. Rijnsdorp showed the spectra having intensity maximum around 54.6 eV for $(Se-Se)^{2-}$ in $NbSe_2Cl_2$ and Nb_3Se_5Cl (8). The spectrum of $I_{0.5}TaSe_4$ has a peak around 55 eV so that the selenium in the compound is probably dimeric and monovalent.

Crystal structure

The systematic extinctions (hkl absent for h+k+l odd) indicate that the space group belongs to I4/mmm, I422, I4mm , I$\bar{4}$m2 or I$\bar{4}$2m. Space group I4/mmm seemed unlikely because the discrepancy factor R was 0.30 even at the end of the anisotropic refinement. Space group I422 was adopted with all atoms in the sites shown in Table 3. Atomic parameters were derived from a

Table 3. Positional and thermal parameters (in 10^{-2} Å^2) of $I_{0.5}TaSe_4$ in space group I422

atom	Ta(1)	Ta(2)	I	Se(1)	Se(2)
site	4c	4d	4e	16k	16k
x	0.	0.	0.	0.54623	0.31167
y	0.5	0.5	0.	0.21657	0.12318
z	0.	0.25	0.15608	0.13242	0.11762
β_{11}	0.00108	0.00071	0.00503	0.00228	0.00128
β_{22}	0.00148	0.00071	0.00503	0.00118	0.00110
β_{33}	0.00188	0.00203	0.00523	0.00145	0.00192
β_{12}	0.	-0.00018	0.	-0.00039	-0.00007
β_{13}	0.	0.	0.	0.00031	0.00072
β_{23}	0.	0.	0.	0.00030	0.00011

Patterson synthesis and refined by a full-matrix least-squares method. The atomic scattering factors were taken from Cromer and Waber (9). At the end of the anisotropic refinement the discrepancy factor R was 0.068 for space group I422. Positional and thermal parameters are summarized in Table 3.

The distance between Se(1) and Se(2) is 2.42 Å as shown in Table 4 expecting the Se covalent radius of 1.16 Å (10). The Se atoms form Se_2^{2-} units and the Ta atoms are coordinated with four Se_2^{2-} as shown in Fig. 4. The shared quadrilateral faces of $Ta(Se_2)_4$ unit rotate by 45° each other as depicted in Fig. 5. The I atoms are located between the $TaSe_4$ chains. To simplify the picture, there are no distinctions between Ta(1) and Ta(2) and also between Se(1) and Se(2) in Fig. 5. Fig. 6 illustrates these site differences. The distance between the I atom and the Se(2)

Table 4. Bonding distances (Å) in $I_{0.5}TaSe_4$

Ta(1) - Ta(2)	3.188
Se(1) - Se(1)	3.490
Se(1) - Se(2)	2.420
Ta(1) - Se(1)	2.707
Ta(1) - Se(2)	2.622
Ta(2) - Se(1)	2.593
Ta(2) - Se(2)	2.734
Se(1) - I	4.814
Se(2) - I	3.239

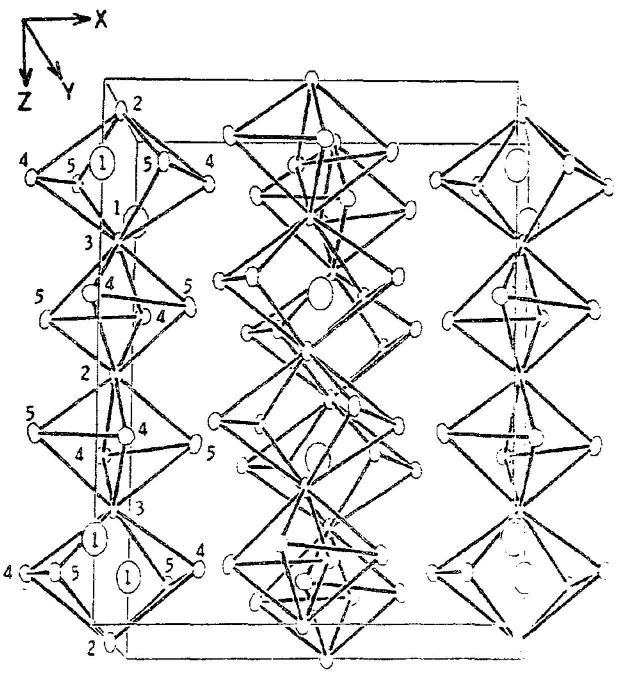

Fig. 4

Stereoscopic view of $I_{0.5}TaSe_4$. The numbers in the figure respectively, 1:I, 2:Ta(1), 3:Ta(2), 4:Se(1), 5:Se(2).

is 3.24Å. It is much shorter than the sum of Van der Waals radii of iodine (2.15Å) and selenium (2.00Å). A comparable distance, 3.78Å, is observed between the iodine and the selenium in trimethyl selenonium iodine, $(CH_3)_3SeI$ (11). The compound was assumed as a charge transfer complex, with the iodine ion acting as a donor, and the selenonium ion as acceptor. Much shorter bonding distances of about 2.8Å are observed on several molecular complexes such as $C_4H_8Se_2\ 2I_2$(12). Weak interaction can be expected between the I

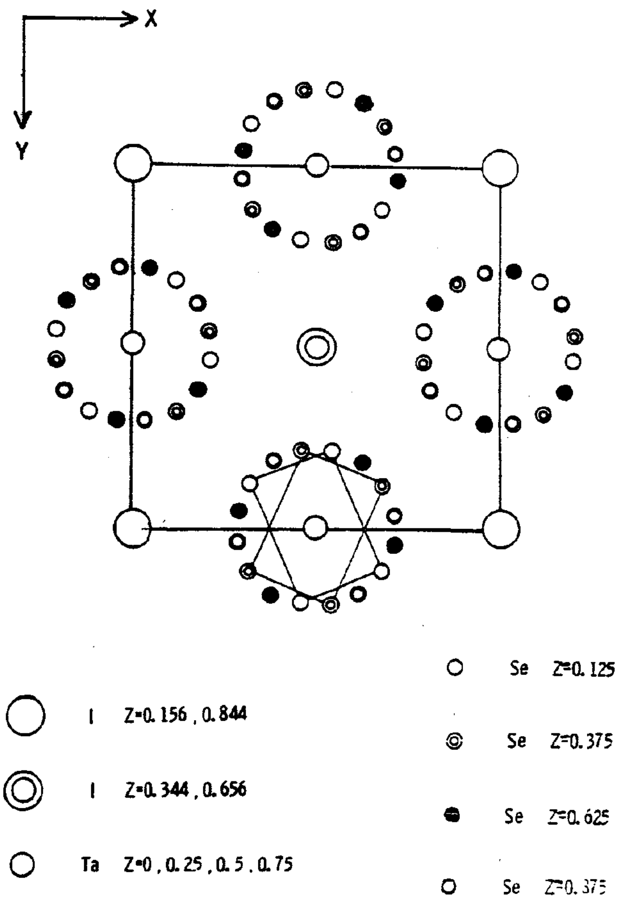

Fig. 5. Crystal structure of $I_{0.5}TaSe_4$ projected on the xy plane

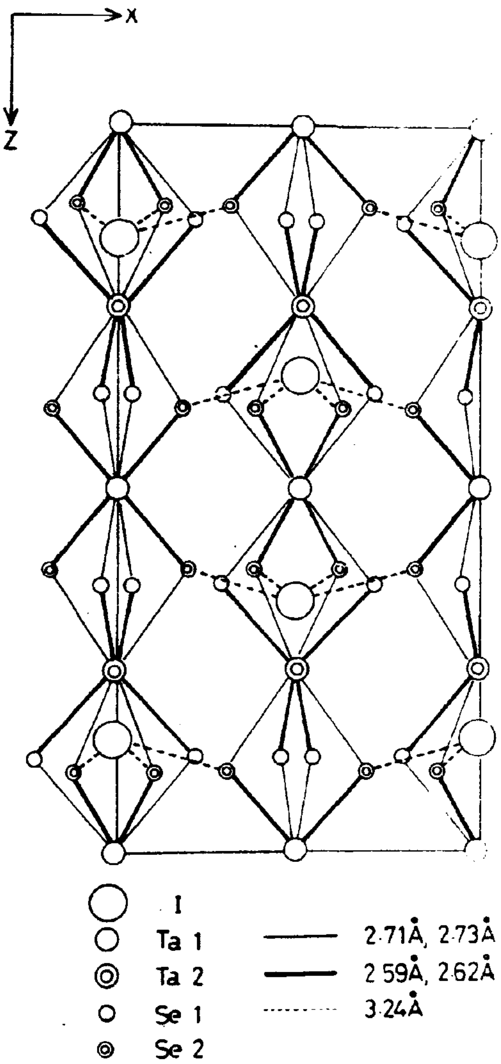

Fig. 6. Schematic crystal structure of $I_{0.5}TaSe_4$ projected on the yz plane

atom and the Se(2) atom in $I_{0.5}TaSe_4$. The distance between the Ta(1) and the Se(2) atoms is 2.62Å. It is comparable to the Ta-Se distances within the $TaSe_6$ trigonal prism, 2.60~2.65Å, suggesting the relatively strong bonding (2). Thus the Ta(1) atom can be expected to donate its electron to the Se(2) atom through the I atom so that it might be Ta^{5+}. On the other hand, the distance between the Ta(2) and the Se(2) is 2.73Å. It corresponds to the distance between Ta and its next nearest neighboring Se belonging to the neighboring $TaSe_6$ units. Thus the interaction between Ta(2) and Se(2) is not so strong. The Ta(2) atom is strongly bound to Se(1) and their bonding distance is 2.59Å.

However, the distance between Se(1) and I is 4.81Å. It is too long for Se(1) and I atoms to make bonding. Thus the Ta(2) atom is tetravalent-like. The Ta(1) and the Ta(2) are alternatively on the $TaSe_4$ chain and $(5d)^1$ electrons localize on the Ta(2) atoms. Fig. 7 shows the way how $TaSe_4$ chains are bonded each other by the charge transfer from the Ta(1) atoms to the I atom through the Se(2) atom. Thus the Ta(1) atoms interact each other in xy planes at level z=0 and at z=0.5 through the bonds to Se(2) and I.

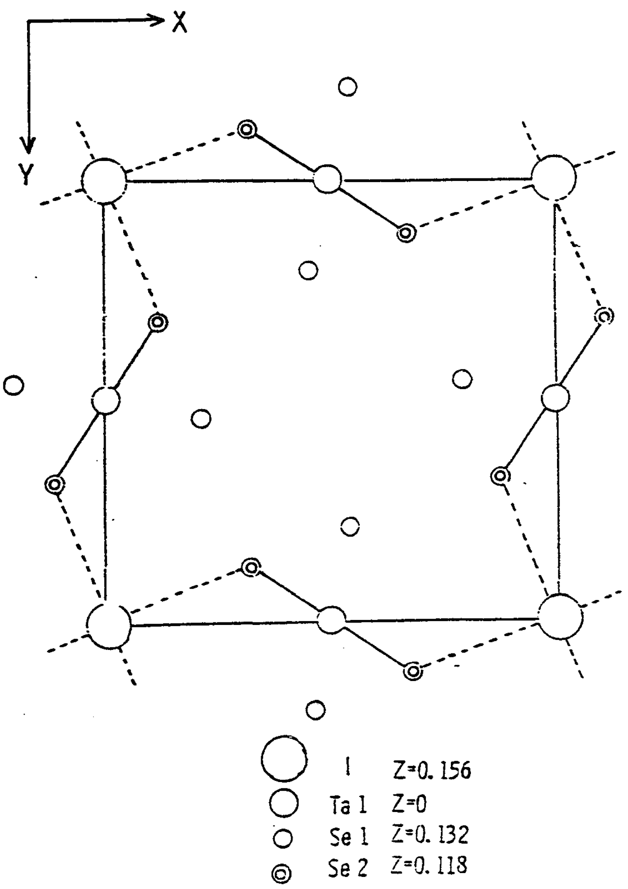

Fig. 7

Cross section of the structure for $I_{0.5}TaSe_4$ at z≈0.125

Preparation and crystal structure of niobium analogue, $I_{0.3}NbSe_4$, were reported (7). The compound is formed by the $NbSe_4$ chains connected each other by charge transfer bond to the interchain iodine. The length of unit cell along c axis is about one and a half times as long as that of $I_{0.5}TaSe_4$. Two kinds of niobium can be distinguishable in the $NbSe_4$ chains. $(4d)^1$ electrons localize on Nb^{4+}. Tetravalent and pentavalent niobiums are in a sequence of Nb^{5+} Nb^{4+} Nb^{4+} Nb^{5+} Nb^{4+} Nb^{4+} Nb^{5+}. The distance is

3.25Å between Nb^{4+} and Nb^{5+}. Weak interaction was assumed to be existed between $(4d)^1$ electrons on Nb^{4+} atoms. Such interaction can not be expected in $I_{0.5}TaSe_4$. A careful measurement of magnetic susceptibility showed an weak temperature dependence due to the resulting localizing $(5d)^1$ electrons on Ta^{4+}.

In summary, the new compound $I_{0.5}TaSe_4$ was obtained by heating the starting mixture having a compositional ratio of Ta:Se:I=1:4:1 in 460°C/420°C temperature gradient for 1 week. The crystal structure is composed of the infinit chains of $TaSe_4$ along c-axis. Iodine is located between the chains. Weak charge transfer interaction is observed between the I atoms and the Se atoms. $(5d)^1$ electrons localize on Ta^{4+} in the infinit $TaSe_4$ chains.

Acknowledgment

Authors wish to express their thanks to Professor F. Kanamaru and his colleague at ISIR in Osaka University for their assistance in structural analysis. One of the author (S. U.) also thank to Mr. H. Yamada at ISIR for his help in ESCA measurement and to Mr. S. Eguchi for the use of X-ray fluorescent spectrometer.

References

1) P. A. Lee (ed.) "Optical and Electrical Properties", "Physics and Chemistry of Materials with Layered Structures" vol. 4, D. Reidel Pub. Co. (1976).

2) F. Hulliger, "Structural Chemistry of Layer-type Phases", F. Lévy (ed.) "Physics and Chemistry of Materials with Layered Structures" vol. 5, D. Reidel Pub. Co. (1976).

3) M. S. Whittingham, Prog. Solid State Chem., 12, 41 (1978).

4) R. Allmann, I. Baumann, A. Kutoglu, H. Rösch and E. Hellner, Naturwissenschaften, 11, 263 (1964).

5) K. Selte and A. Kjekshus, Acta Chem. Scand., 18, 697 (1964).

6) L. Guémas, A. Meerschaut and P. Palvadeau, C. R. Acad. Sci., 281, 297 (1975).

7) A. Meerschaut, P. Palvadeau and J. Rouxel, J. Solid State Chem., 20, 21 (1977).

8) J. Rijnsdorp, Thesis, Groningen (1978).

9) D. T. Cromer and J. T. Waber, Acta Cryst., 18, 104 (1965).

10) L. Pauling, "The Nature of the Chemical Bond", Ithaca, Cornell Univ. Press (1960).

11) H. Hope, Acta Cryst., 20, 610 (1966).

12) A. F. Wells, "Structural Inorganic Chemistry" 4th ed. pp. 600, Clarendon Press, Oxford (1975).

* Dr.A. Meershaut informed us on this meeting that he has published the crystal structure of $I_{0.5}TaSe_4$ on Acta Cryst. B38,2877 (1982). He kindly allowed to publish our paper in this proceeding because it contains some chemical merits.